# AMENDMENT NO. 2 MARCH 2010
# TO
# IS 4032 : 1985 METHOD OF CHEMICAL ANALYSIS OF HYDRAULIC CEMENT

***( First Revision )***

(*Page* 4, *clause* **2.1**) — Insert the following at the end:

'**2.2 Preparation of Sample for Analysis** — Keep about 10 g sample in a large glass Petri dish and spread it evenly into a thin layer. Put it in the oven maintained at 105 ± 5°C for one hour to remove any superficially adsorbed moisture. Take it out and keep in a desiccator and cool it to room temperature for chemical analysis.'

(*Page* 7, *clause* **4.1.20**) — Insert the following at the end:

'**4.1.21** *Nitrobenzene* ,

**4.1.22** *Potassium Chromate Indicator* — Dissolve 0.2 g in 100 ml of distilled water.

**4.1.23** *Silver Nitrate Solution* — 0.025 N. Dry silver nitrate at 120°C for two hours and allow to cool in a desiccator. Weigh out accurately 4.246 7 g in a 250 ml beaker, dissolve in little quantity of distilled water and transfer in a one-litre volumetric flask and make up to the mark.

**4.1.23.1** *Standardization of 0.025 N silver nitrate solution* — Silver nitrate may be standardized to check its normality by titrating with a standard solution of 0.025 N sodium chloride.

*Preparation of 0.025 N Sodium Chloride* — Dry sodium chloride at 600 ± 50°C for 50 min and cool in a desiccator. Weigh 1.461 5 g in a 250-ml beaker. Dissolve in about 50 ml water. Transfer in a one-litre volumetric flask and make up to one litre.

Take 10 ml of 0.025 N sodium chloride solution in a 250-ml conical flask. Add 2 ml of potassium chromate indicator. Titrate with silver nitrate solution to slight brick red colour end point. The exact normality of silver nitrate may be

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calculated using the equation:

$$N_1V_1 = N_2V_2$$

where

$N_1$ = normality of sodium chloride that is 0.025,
$V_1$ = 10 ml,
$N_2$ = normality of silver nitrate solution, and
$V_2$ = volume of silver nitrate required.

**4.1.24** *Ferric Alum Indicator* — A saturated solution of ammonium iron (III) sulphate dodecahydrate [$NH_4Fe(SO_4)12H_2O$] in distilled water (about 40 percent) is made, to which few drops of 6 N nitric acid are added. 1 ml of this is used in the titration.

**4.1.25** *Ammonium Thiocyanate Solution* — 0.025 N. Weigh accurately 1.903 0 g in a 250-ml beaker, dissolve in about 50 ml water and transfer in a one-litre volumetric flask. Make up to one litre. This solution needs standardization with standard silver nitrate solution.

**4.1.25.1** *Standardization of ammonium thiocyanate solution* — Pipette 20 ml of standard 0.025 N silver nitrate solution into a 250-ml conical flask, add 5 ml of 6 N nitric acid and 1 ml of ferric alum indicator. Run in the ammonium thiocyanate solution from a burette. At first a white precipitate is produced, rendering the liquid a milky appearance and as each additional drop of thiocyanate falls in, it produces a reddish-brown cloud, which quickly disappears on shaking. As the end point approaches, the precipitate becomes flocculent and settles easily; finally one drop of the thiocyanate solution produces a faint brown colour, which no longer disappears upon shaking. This is the end point. It is essential to shake vigorously during titration in order to obtain correct results, because the freshly precipitated silver thiocyanate formed during the titration adsorbs silver ions, thereby causing a false end point, which however, disappears with vigorous shaking. Calculate the normality of the thiocyanate solution by using the normality equation:

$$N_3V_3 = N_4V_4$$

where

$N_3$ = normality of silver nitrate that is 0.025,
$V_3$ = 20 ml,
$N_4$ = normality of ammonium thiocyanate, and
$V_4$ = volume of ammonium thiocyanate required.

(*Page* 7, *clause* **4.2**) — Substitute the following for the existing:

'**4.2 Loss on Ignition** — Heat about 1 g of oven-dried sample, $m_1$ (accurately weighed up to four decimal places) for 15 min in a weighed and covered platinum crucible (a porcelain crucible may also be used) of 20 to 25 ml capacity by placing it in a muffle furnace at a temperature of 950 ± 25°C; cool and weigh. Check the loss in weight by a second heating for 5 min and reweigh ($m_2$). Calculate the loss on ignition as below:

$$\text{Percent loss on ignition} = \frac{(m_1 - m_2) \times 100}{m_1}$$

Round off the calculated value and report up to 1 decimal place.'

(*Page* 7, *clause* **4.3.1**, *line* 1) — Substitute 'Transfer about 0.5 g - 1.0 g, $W$ (accurately weighed up to four decimal places) of oven dried sample' *for* 'Transfer 0.5 g of the sample'.

(*Page* 8, *clause* **4.3.4**) — Substitute the following for the existing formula:

$$\text{'Silica, percent} = \frac{(W_1 - W_2) \times 100}{W},$$

(*Page* 9, *clause* **4.4.3.1**) — Substitute the following for the existing formula:

$$\text{'}R_2O_3\text{, percent} = \frac{\text{Weight of residue} \times 100}{W},$$

(*Page* 12, *clause* **4.7.1.2**) — Substitute the following for the existing formula:

$$\text{'CaO, percent} = \frac{\text{Weight of residue} \times 100}{W},$$

(*Page* 13, *clause* **4.8.1.1**) — Substitute the following for the existing:

$$\text{'MgO, percent} = \frac{W_1 \times 36.22}{W}$$

where

$W_1$ = grams of residue ($Mg_2P_2O_7$), and

36.22 = molecular ratio of 2 MgO to $Mg_2P_2O_7$ (0.362 2) × 100'

(*Page* 21, *clause* **4.12.3.1**) — Insert the following at the end:

'**4.13 Chloride**

**4.13.1** The sample is boiled with dilute nitric acid, thereby dissolving all the chlorides present. Excess standard silver nitrate solution is added to it. The chlorides react with silver nitrate forming silver chloride. Excess of silver nitrate is then back titrated with standard ammonium thiocyanate solution. Ferric alum is used as an indicator which gives reddish-brown colour at the end point. The reactions involved are:

$$Ag^{+} + Cl^{-} = AgCl$$

$$Ag^{+} + SCN^{-} = Ag\,SCN$$

When the reactions are complete, the slightest excess of thiocyanate produces a reddish-brown colouration due to the formation of complex ferric-thiocyanate ion:

$$Fe^{+++} + SCN = [FeSCN]^{++}$$

**4.13.2** *Procedure*

**4.13.2.1** Dry the sample at 110°C for 1 hour and cool in a desiccator. Take 2 g of sample accurately weighed up to fourth decimal place in a 250-ml beaker. Add about 40 ml of distilled water and 10 ml concentrated nitric acid. Heat to boil and shake thoroughly. Keep for few minutes to settle and then filter through Whatman No. 40 filter paper in a conical flask. Wash the filter paper along with its contents 4-5 times with hot distilled water. Reject the insoluble in the funnel. To the filtrate add 2 ml of nitrobenzene and 10 ml 0.025 N silver nitrate solution with the help of a micro burette. Then add 1 ml of ferric alum indicator. Titrate with 0.025 N ammonium thiocyanate solution to get a faint brown colour as described in **4.1.25.1**. Note down the volume of ammonium thiocyanate used.

As the reagents and distilled water, etc, used in the exercise may contain some chloride as an impurity, it is essential to subtract this to get the actual chloride content in the sample. For this a blank run is done as given in **4.13.2.2**.

**4.13.2.2** *Blank* — Take 100 ml distilled water in a conical flask. Add 10 ml concentrated nitric acid + 10 ml 0.025 N silver nitrate solution, 2 ml nitrobenzene and 1 ml ferric alum. Titrate with 0.025 N ammonium thiocyanate solution.

Let ammonium thiocyanate required be $y$ ml

Blank = $(10 - y)$ ml

**4.13.3** *Calculation*

Let ammonium thiocyanate used in the sample titration be $x$ ml

Silver nitrate consumed by the chlorides, $Z = [10 - (10 - y) - x]$ ml

$$\text{Percent chloride, Cl} = \frac{Z \times 0.035\,46 \times 0.025 \times 100}{\text{Mass of sample}}$$

NOTE — The calculation is based on the normalities of silver nitrate and ammonium thiocyanate to be exactly same, that is, 0.025. In case the normalities differ, then correction may be applied using appropriate factor.

**4.13.4** *Repeatability and Reproducibility*

The standard deviation of repeatability of the method is 0.005 percent. The standard deviation of reproducibility is 0.010 percent.'

(*Page* 34, *clause* **6.12.3**) — Insert the following at the end:

'**6.13** The method for determining chloride content in Portland slag cement shall be the same as described in **4.13**.'

(*Page* 36, *clause* **7.4**) — Insert the following at the end:

'**7.5** The method for determining chloride content in Portland slag cement shall be the same as described in **4.13**.'

(CED 2)

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